

JAPANESE

[JP,2001-019827,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR  
ART EFFECT OF THE INVENTION TECHNICAL PROBLEM  
MEANS

[Translation done.]

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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the thermoplastic elastomer composition which can be used as a raw material of the various molded products which the mold-goods surface got damaged at, and were excellent in the sex (scratch-proof nature), and were excellent in pliability, heat resistance, the low-temperature characteristic, weatherability, intensity, and molding workability.

[0002]

[Description of the Prior Art]Many thermoplastic elastomer which excels [ use / the autoparts whose vulcanized gum was in use, household appliance parts, a medical department article, and / general-merchandise ] in productivity is used increasingly conventionally. An olefin system elastomer, a polyurethane elastomer, soft polyvinyl chloride, etc. which consist of ethylene propylene rubber and polypropylene as these examples are mentioned.

[0003]However, the actual condition is that these molding materials have a fault in respect of scratch-proof nature, pliability, processability, economical efficiency, and recycling efficiency, respectively. That is, an olefin system elastomer is comparatively cheap and inferior to the pliability of what is excellent in weatherability and heat resistance, and scratch-proof nature. Although a polyurethane elastomer is excellent in

scratch-proof nature, it is inferior to pliability and weatherability, and it has the fault of being expensive. Although elasticity VCM/PVC is comparatively cheap and being excelled in weatherability and scratch-proof nature, it has the fault of being inferior to the pliability in low temperature, and recycling efficiency.

[0004]Some proposals are made also about the elastomer composition using the hydrogenation derivative (it is hereafter written as a hydrogenation block copolymer) of the vinyl aromatic compound-conjugated diene compound block copolymer. For example, the constituent which blended the softener for rubbers and olefin system resin with the hydrogenation block copolymer is indicated by JP,50-14742,A, JP,52-65551,A, and JP,58-206644,A each gazette. However, scratch-proof nature is inferior in these constituents as well as an olefin system elastomer.

[0005]

[Problem(s) to be Solved by the Invention]This invention employing efficiently the characteristic of a hydrogenation block copolymer of it having been made against the background of said conventional technical problem, and having excelled in pliability, weatherability, heat resistance, the low-temperature characteristic, intensity, and molding workability. The thermoplastic elastomer composition which improved scratch-proof nature can be provided, and the elastomer composition can be used conveniently for exterior parts etc. among the unnecessary cars of surface coating.

[0006]

[Means for Solving the Problem]Namely, hydrogenation diene system copolymer:100 weight section (b) which hydrogenates a copolymer of a vinyl aromatic compound and a conjugated diene compound in which this invention has a random copolymer block of a vinyl aromatic compound of at least one (a), and a conjugated diene compound, (b-1) polypropylene system polymer (propylene is included 85% of the weight or more): -- 10 to 60-% of the weight (b-2) ethylene-propylene system copolymer rubber (propylene is included 75 or less % of the weight): -- it being 40 to 90% of the weight of a mixture, and, Mean-dispersion particle diameter of ethylene-propylene system copolymer rubber 2 micrometers or less, A flexural modulus of this mixture is an elastomer composition in which 20 - 700MPa and Shore D hardness are characterized by a thing, five to polypropylene mixture:900 weight section and \*\* and others 20-60, and whose melt flow rate are 1-60g/10 minutes.

[0007]Hereafter, this invention is explained in detail. The (a) ingredient of this invention is a hydrogenation diene system copolymer which hydrogenates a copolymer of a vinyl aromatic compound and a conjugated diene compound which have at least one random copolymer block of a vinyl aromatic compound and a conjugated diene compound.

[0008](a) As a desirable vinyl aromatic compound which constitutes an ingredient, Styrene, t-butylstyrene, alpha-methylstyrene, p-methylstyrene, Divinylbenzene, 1,1-diphenylstyrene, N,N-dimethyl- p-friend NOECHI styrene, N,N-diethyl- p-aminoethyl styrene,

vinylpyridine, etc. are mentioned, and it is styrene and alpha-methylstyrene more preferably, and these are independent, or are mixed and used. As desirable conjugated diene, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-PENDA diene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, 4,5-diethyl-1,3-octadiene, 3-butyl-1,3-octadiene, and chloroprene are mentioned, it is 1,3-butadiene, isoprene, and 1,3-pentadiene more preferably, and they are 1,3-butadiene and isoprene most preferably.

[0009](a) Desirable weight ratios of the vinyl aromatic compound/conjugated diene in total monomers in an ingredient are 5 / 95 - 60/40, and are 7 / 93 - 50/50 still more preferably. It becomes easy to block when a vinyl aromatic compound pelletizes a hydrogenation diene system copolymer obtained by a mechanical strength, processability, and heat resistance being inferior in less than 5 % of the weight. When vinylaromatic series exceeds 60 % of the weight, it becomes resin-like and a shock-resistant family name, pliability, the low-temperature characteristic, and transparency are inferior.

[0010](a) Quantity of a conjugated diene part which has the desirable vinyl bonds before hydrogenation of an ingredient is not less than 60% most preferably not less than 40% still more preferably exceeding 20%. In 20% or less, the flexible improvement effect at the time of blending to polyolefin system resin falls. A hydrogenation rate of a double bond of a conjugated diene part is not less than 80%, and is not less than 95% still more preferably not less than 90% preferably. At less than 80%, transparency, heat resistance, weatherability, and a mechanical strength are inferior, and it is not desirable.

[0011](a) a number average molecular weight of an ingredient -- 50,000-700,000 -- they are 80,000-500,000, and a hydrogenation diene system polymer that are 100,000-300,000 still more preferably preferably. When it becomes easy to block when a number average molecular weight pelletizes a hydrogenation diene system copolymer obtained by less than 50,000, and also it blends with other resin, a mechanical strength and molding appearance are inferior, and processability is inferior when 700,000 is exceeded.

[0012]Molecular weight distribution [ratio (Mw/Mn) of weight average molecular weight (Mw) and a number average molecular weight (Mn)] of a hydrogenation block copolymer is 1.5 or less still more preferably two or less preferably five or less. If molecular weight distribution exceeds 5, intensity of an elastomer composition and heat resistance are not enough, and preferred.

[0013]A molecular weight and molecular weight distribution given [ this ] in a specification are measured, for example by the GPC (Gel Permeation Chromatography) method. In GPC analysis, a molecular weight is calculable using an analytical curve prepared with standard polystyrene.

[0014](a) As an ingredient, it is the hydrogenation diene system copolymer according to claim 2 preferably, and an elastomer composition which was excellent in a sex with a crack-proof, pliability, and heat resistance much more is obtained, holding more highly the

outstanding feature of polyolefin system resin original [, such as a mechanical strength and a moldability, ], if this is used. Explanation of the (a) ingredient of the following this inventions is given an example, and explains a hydrogenation diene system copolymer shown in claim 2.

[0015](a) The (A) block in an ingredient is a block which hydrogenates a polymeric block which made a vinyl aromatic compound a subject, and may carry out copolymerization of the vinyl compound copolymerizable otherwise 10 or less % of the weight still more preferably 10 or less % of the weight preferably.

[0016](A) total monomers from which a desirable joint content of a vinyl aromatic compound under block constitutes the (a) ingredient -- at least -- 3- it is 5 to 30 % of the weight still more preferably 40% of the weight. (A) A joint content of vinylaromatic series of a block by less than 3% of the weight of total monomers. When it becomes easy to block when a hydrogenation diene system copolymer obtained by heat resistance and a mechanical strength being inferior is pelletized, and also it blends with other ingredients, processability is inferior, and when it, on the other hand, exceeds 40 % of the weight, transparency, pliability, processability, and the low-temperature characteristic are inferior.

[0017](B) A block is a block which hydrogenates a random copolymer block of a vinyl aromatic compound and conjugated diene. (B) 2- of total monomers from which a desirable joint content of a vinyl aromatic compound under block constitutes the (a) ingredient -- it is 6 to 30 % of the weight still more preferably four to 40% of the weight preferably 50% of the weight.

[0018]A desirable content of the (A) block in the (a) block copolymer of 3 to 50 % of the weight of (A) blocks is 5 to 40 % of the weight more preferably. It is at [however, (A)+(B) =100 % of the weight].

[0019]A polymeric block (A) which a hydrogenation copolymer used by this invention makes at least one vinyl aromatic compound with a subject, It is a block copolymer which hydrogenates a block copolymer which consists of at least one random copolymer block (B) of a vinyl aromatic compound and a conjugated diene compound, For example, B, A-B, A-B-A, B-A-B-A, A-B-A-B-A, B-A-B-A-B, [A-B] l-X, or [A-B-A] l-X [A and B are the same as the above (A) and the (B) block among a formula. l shows an integer of 2-4 and X shows coupling agent residue. ] It has the structure of \*\*.

[0020]A polymeric block (A) which makes a subject a vinyl aromatic compound of a hydrogenation block copolymer used as a (a) ingredient by this invention, A random copolymer block (B) of a vinyl aromatic compound and a conjugated diene compound, distribution of a vinyl aromatic compound in each polymeric block or a conjugated diene compound -- tapered (that in which a chain is met, and a monomer component increases or decreases) one -- or it being block like shape or such arbitrary combination in part, and, When there are the two or more polymeric blocks (A) and (B), respectively, each may be the same structure and each polymeric block may be a different structure.

[0021]If these block copolymers have the above-mentioned structure, they will not be what restricts the manufacturing method, For example, a

vinyl aromatic compound-conjugated diene compound block copolymer before hydrogenation is compoundable in an inert solvent by a method indicated to JP,40-23798,B, JP,3-72512,A, etc. using a lithium catalyst. [0022]As a manufacturing method of hydrogenation, a method of JP,42-8704,B, JP,43-6636,B, JP,60-220147,A, JP,61-33132,A, or JP,62-207303,A is mentioned, for example. as for an aliphatic double bond originating in a conjugated diene compound in that case, hydrogenation of the not less than 90% is carried out preferably at least 80% -- on the other hand -- a vinyl aromatic compound -- less than 20%, it is chosen so that hydrogenation of the less than 10% may be carried out preferably. About a hydrogenation rate of the above-mentioned hydrogenation block copolymer, it can know easily by an infrared spectroscopic analysis or nuclear magnetic resonance analysis.

[0023]Unlike a mixture by polypropylene of the former [ mixture / which is the (b) ingredient of this invention / polypropylene ], an extrusion machine with EP rubber etc., Brabender, etc., a polyolefin elastomer in which a mixture is formed simultaneously with a polymerization and which has a plasto-elasticity is suitably used in a reactor. Since a rubber phase formed is distributed minutely and uniformly in a polypropylene matrix, this mixture is excellent in scratch-proof nature compared with a mixture by the conventional blend. Therefore, when it adds to a thermoplastic elastomer composition of this invention, scratch-proof nature and pliability are not spoiled but it has a role which raises molding workability and molding appearance (flow mark).

[0024]A polypropylene mixture which is the (b) ingredient of this invention is a propylene copolymer mixture obtained by at least two or more steps of successive polymerization, for example. In the first process, polymerize a copolymer (propylene is included 85% of the weight or more) or an ethylene propylene copolymer (propylene is included 85% of the weight or more) of a homopolymer or propylene, and alpha olefin of propylene, and an ingredient (b-1) is generated, After the following process, ethylene-propylene (propylene is included 75 or less % of the weight) or an ethylene-propylene-alpha olefin (a small amount of diene may also be included) copolymer (propylene is included 75 or less % of the weight) is polymerized, and an ingredient (b-2) is generated.

[0025]An isotactic index of polypropylene obtained a polymerization of propylene of the first process Not less than 80%, It can carry out not less than 85% preferably under existence of ethylene of quantity which is not less than 90% still more preferably or alpha olefin, for example, butene-1, the pentene- 1, 4-methyl-pentene- 1, the hexene- 1 and the octene- 1, or those combination.

[0026]Since ethylene propylene rubber after the second process or an ethylene-propylene-alpha olefin copolymer is polymerized. Monomers to be used are propylene, ethylene, and/or alpha olefin (for example, butene-1, the pentene- 1, 4-methyl-pentene- 1, the hexene- 1 and the octene- 1, or they should put together). A polymerization of a copolymer after the second process can be performed under existence of diene which is not conjugate or conjugate, for example, butadiene, 1,4-hexadiene, 1,5-

hexadiene, and the \*\*\*\*\*- norbornene 1. Diene is 0.5 to 10 % of the weight to weight of total monomers typically used after the second process, when it exists.

[0027]Quantity of (b-2) of quantity of (b-1) in a polypropylene composition of an ingredient (b) is 50 to 85 % of the weight preferably 40 to 90% of the weight 15 to 50% of the weight ten to 60% of the weight.

[0028]The total amount of ethylene by which copolymerization was carried out into a polypropylene mixture of an ingredient (b) is 20 to 35 % of the weight still more preferably 17 to 45% of the weight preferably 15 to 60% of the weight. Quantity of all the alpha olefins by which copolymerization was carried out into a polypropylene mixture of (b) is 5 to 10 % of the weight still more preferably three to 20% of the weight preferably zero to 30% of the weight.

[0029]When a mixture (b) is measured by differential scanning analytical calorimetry (DSC), it shows at least one melting peak which exists at a temperature higher than 120 °C and a desirable temperature higher than 140 °C. a mixture (b) -- the rate 20 of bending flexibility - 700MPa -- desirable -- 50 - 300MPa -- further -- this -- better -- °C is 70 - 200MPa. the Shore D hardness of a mixture (b) -- 20-60 -- it is 30-50 preferably.

[0030]A melt flow rate of a mixture (b) (value measured according to ASTM D1238, 230 °C, and 2.16 kg loads.) following MFR -- outlining -- 1-60g/10 minutes -- desirable -- 5-50g/10 minutes -- they are 10-40g/10 minutes still more preferably for 10 minutes. MFR is not preferred at that (generating of the flow mark) in which melt viscosity of an elastomer composition is high, and the molding workability (mobility) of an elastomer composition falls to in 1g/less than 10 minutes, and appearance of mold goods gets worse. Since the scratch-proof nature of an elastomer composition also falls in 1g/less than 10 minutes, MFR is not preferred. On the other hand, since intensity of an elastomer composition and heat resistance will fall if MFR exceeds 60g/10 minutes, it is not desirable.

[0031]2 micrometers or less of mean-dispersion particle diameter of ethylene-propylene system copolymer rubber distributed in a mixture (b) are 1.5 micrometers or less preferably. If mean-dispersion particle diameter of rubber exceeds 2 micrometers, since the scratch-proof nature of an elastomer composition will fall extremely, it is not desirable.

[0032]A catalyst used for a polymerization of a polypropylene mixture of an ingredient (b) is a Ziegler-Natta catalyst. A desirable catalyst is a resultant with a solid catalyst component, a trialkylaluminum compound, and an electron donor compound (external donor) containing a titanium compound and an electron donor compound (internal donor) which were supported on a magnesium chloride. As an adjustment method of a catalyst, and a polymerization method of an ingredient (b), JP,3-205439,A, JP,6-25367,A, JP,6-25489,A, etc. are mentioned, for example.

[0033]Loadings of a polypropylene mixture of an ingredient (b) in a thermoplastic elastomer composition of this invention are 15 - 200 weight section still more preferably ten to 500 weight section preferably five to 900 weight section to hydrogenation block copolymer (a)100

weight section. If loadings of a polypropylene mixture of an ingredient (b) exceed 900 weight sections, rubber elasticity falls and it is not desirable. Loadings of a polypropylene mixture of an ingredient (b) are not preferred at that (the flow mark occurs) in which molding appearance of a thermoplastic elastomer composition gets worse in less than five weight sections.

[0034]As a polypropylene mixture of an ingredient (b) used for this invention, it can obtain easily under the name of Adflex, Hifax (a product made by Montell, Catalloy TPO series), etc.

[0035]The constituent of this invention can add a hydrocarbon oil by request. A hydrocarbon oil has the effect of improving the pliability of a constituent obtained, and processability, and straight mineral oil of a non-aromatic system, or liquefied or a synthetic softener of low molecular weight is suitable. Although paraffin series oil and naphthene system oil which are generally known can be used as straight mineral oil of a non-aromatic system, 10 or less % of the weight of paraffin series oil has an especially preferred aromatic ring ingredient.

[0036]Loadings of a hydrocarbon oil are zero to 60 weight section still more preferably zero to 100 weight section preferably zero to 200 weight section to hydrogenation block copolymer 100 weight section. Since the scratch-proof nature of an elastomer composition and heat resistance will fall if loadings of a hydrocarbon oil exceed 200 weight sections, it is not desirable.

[0037]To a constituent of an invention, polyolefin system resin can be added by request. As poly OREFION system resin which can be added, polyethylene resin, polypropylene resin, etc. are specifically raised. As polyethylene resin, a copolymer of low density polyethylene, straight-chain-shape low density polyethylene, high density polyethylene, ethylene, and alpha olefin of the carbon numbers 3-8, etc. are raised. In the case of a copolymer of ethylene and alpha olefin of the carbon numbers 3-8, as alpha olefin in a copolymer, propylene, butene-1, isobutene, the pentene- 1, the hexene- 1, 4-methylpentene- 1, and octene-1 grade are raised. As for a rate of alpha olefin, 30 or less % of the weight of a thing is used.

[0038]As polypropylene resin, it is a copolymer with a propylene homopolymer or propylene, ethylene, or alpha olefin of the carbon numbers 3-8 (it is written as propylene resin below). In the case of a copolymer with propylene, ethylene, or alpha olefin of the carbon numbers 3-8, as alpha olefin in a copolymer, butene-1, isobutene, the pentene- 1, the hexene- 1, 4-methylpentene- 1, and octene-1 grade are raised. As for a rate of ethylene or alpha olefin, 30 or less % of the weight of a thing is used. A copolymer with random, propylene of a block and ethylene, or alpha olefin is raised. [ a propylene homopolymer which can compound these propylene resin by a publicly known method conventionally for example, is compounded using a Ziegler-Natta catalyst, ] It is more desirable to use a polypropylene resin as polyolefin system resin, in order to obtain an elastomer composition which is excellent in heat resistance and a moldability. MFR of these polyolefin system resin -- 1-100g/-- they are 5-60g/10 minutes preferably for 10



minutes. MFR is not preferred at that (generating of the flow mark) in which melt viscosity of an elastomer composition is high, and the molding workability (mobility) of an elastomer composition falls to in 1g/less than 10 minutes, and appearance of mold goods gets worse. Since intensity of an elastomer composition and heat resistance will fall if MFR exceeds 100g/10 minutes, it is not desirable.

[0039]it has the effect of hardness of a thermoplastic elastomer composition adjusting these polyolefin system resin, and improving processability, and loadings are zero to 80 weight section still more preferably zero to 110 weight section preferably zero to 150 weight section to hydrogenation block copolymer 100 weight section.

[0040]Furthermore, a constituent of this invention may add an inorganic bulking agent, stabilizer, lubricant, colorant, a silicone oil, fire retardant, etc. if needed. As an inorganic bulking agent, calcium carbonate, talc, magnesium hydroxide, mica, barium sulfate, a silicic acid (white carbon), titanium oxide, carbon black, etc. are mentioned, for example. As stabilizer, a hindered phenolic antioxidant, a \*\*\*\* system thermostabilizer, a hindered amine light stabiliser, a benzotriazol system UV absorbent, etc. are mentioned. As lubricant, stearic acid, stearic acid ester, metal salt of stearic acid, etc. are mentioned.

[0041]Generally, as a method of manufacturing an elastomer composition of this invention, in order to blend a polymer component, what kind of method known for conventional technology may be used. In order to obtain the most homogeneous mixed material, a method of carrying out melt kneading using various kinds of kneading machines like a roll mill usually used, a kneader, a Banbury mixer, and an extrusion machine is desirable. Before carrying out melt kneading, a Henschel mixer, a tumbler, and a mixer like a ribbon blender are used, the dry blend of these compounds is carried out beforehand, and a homogeneous elastomer composition is obtained by carrying out melt kneading of this mixture.

[0042]As a fabricating-operation method of an elastomer composition of this invention, injection molding, extrusion molding, compression molding, etc. can be adapted.

[0043]Since this elastomer composition is excellent in a sex with a crack-proof, pliability, the low-temperature characteristic, weatherability, intensity, and molding workability, It can be used as important elastomer parts of appearance. For example, various handles of exterior parts and home electronics, a skin material, a bumper, a hose, etc. can be conveniently used as alternate material of elasticity PVC among the malls of a car, a skin material (sheet), a change speed lever knob, a handle, a doorknob, etc.

[0044]

[Embodiment of the Invention]In an example and a comparative example, the examining method used for various kinds of valuation methods is as follows.

[0045](1) Hardness [-] It measures at :JIS K6253, A type, and 23 \*\*.

(2) The tensile strength [kgf/cm<sup>2</sup>]:JIS K 6251 or No. 3 dumbbell and the sample used the press sheet of 2-mm thickness.



(3) The elongation [%]:JIS K 6251 or No. 3 dumbbell and the sample used the press sheet of 2-mm thickness.

(4) Impact resilience [%] It measured in :JIS K6255, the Lubke pendulum type, g/23 \*\* (5) melt-flow-rate (MFR) [10-minute]:ASTM D1238, 230 \*\*, and 2.16 kg loads.

[0046](6) A sex with a crack-proof, gloss retention [%] : the plate of the surface smooth with injection molding was fabricated. The plate was placed horizontally, the cheesecloth which added load 40 g/cm<sup>2</sup> was placed, and it was made to go back and forth 200 times. The degree of brilliancy of the friction surface was measured by the method of JISK7105 (E1), and retention;(E1/E0) x100 (%) from the degree of brilliancy (E0) before friction was calculated.

[0047](7) Crimp omission examination : the plate of the surface crimp (crepe, an edging depth of about 20 microns) was fabricated in injection molding. The plate was neglected in 100 \*\* oven for 168 hours. After taking out from oven, the surface state was observed visually and that to which \*\* and gloss came out of that to which gloss came out of that changeless O and a little was made into x.

[0048](8) Molding workability : 70 mm in width, 130 mm in length, 2 mm in thickness, and a side gate plate were fabricated with the injection molding machine on the following conditions. Appearance, such as the flow mark and gloss, was visually observed for the Plastic solid, O and a little poor thing were made into \*\*, and the poor thing was made into x for the good thing.

[0049]Cylinder-temperature C1:200 \*\*, C2:210 \*\*, C3:210 \*\*, nozzle-temperature:200 \*\*, an injection-speed:low speed, a die temperature: Each ingredient used by the example and the comparative example 40 \*\* again is as follows.

[0050]An ingredient (a)-1 A-B[styrene polymer block (A), the random copolymer block (B) of styrene and conjugated diene, In (a)-1 - 6, have the structure of the same], and The number average molecular weight 130000, molecular weight distribution 1.1, 35 % of the weight of the total amounts of combined styrene, (a) 60% in 35 % of the weight of the total amounts of styrene by which the amount of styrene by which the content of the inner (A) block is contained during a block (A) 35% of the weight is contained in (a), The amount of 1,2-vinyl bonds of the polybutadiene part before hydrogenation compounded the hydrogenation block copolymer of the styrene / butadiene block copolymer which is 99% of a hydrogenation rate of a polybutadiene part 75% of the weight by the method indicated to JP,60-220147,A.

[0051]Have the structure of ingredient (a)-2 A-B-A, and The number average molecular weight 150000, molecular weight distribution 1.1, 15 % of the weight of the total amounts of combined styrene, (a) 50% in 18 % of the weight of the total amounts of styrene by which the amount of styrene by which the content of the inner (A) block is contained in a block (A) 18% of the weight is contained in (a), The amount of 1,2-vinyl bonds of the polybutadiene part before hydrogenation compounded the hydrogenation block copolymer of the styrene / butadiene block copolymer which is 99% of a hydrogenation rate of a polybutadiene part

76% of the weight by the method indicated to JP,60-220147,A.

[0052]Have the structure of ingredient (a)-3 A-B-A, and The number average molecular weight 280000, molecular weight distribution 1.2, 25 % of the weight of the total amounts of combined styrene, (a) 60% in 25 % of the weight of the total amounts of styrene by which the amount of styrene by which the content of the inner (A) block is contained in a block (A) 21% of the weight is contained in (a), The amount of 1,2-vinyl bonds of the polybutadiene part before hydrogenation compounded the hydrogenation block copolymer of the styrene / butadiene block copolymer which is 99% of a hydrogenation rate of a polybutadiene part 77% of the weight by the method indicated to JP,60-220147,A.

[0053]Have the structure of ingredient (a)-4 A-B-A, and The number average molecular weight 135000, molecular weight distribution 1.2, 31 % of the weight of the total amounts of combined styrene, (a) 60% in 31 % of the weight of the total amounts of styrene by which the amount of styrene by which the content of the inner (A) block is contained in a block (A) 36% of the weight is contained in (a), 3 of the polyisoprene part before hydrogenation and 4-coupling amount compounded the hydrogenation block copolymer of the styrene / isoprene block copolymer which is 99% of a hydrogenation rate of a polyisoprene part 65% of the weight by the method indicated to JP,60-220147,A.

[0054]Have the structure of ingredient (a)-5 B-A-B-A, and The number average molecular weight 160000, molecular weight distribution 1.1, 35 % of the weight of the amounts of combined styrene, (a) 50% in 35 % of the weight of the total amounts of styrene by which the amount of styrene by which the content of the inner (A) block is contained in a block (A) 40% of the weight is contained in (a), The amount of 1,2-vinyl bonds of the polybutadiene part before hydrogenation compounded the hydrogenation block copolymer of the styrene / butadiene block copolymer which is 99% of a hydrogenation rate of a polybutadiene part 78% of the weight by the method indicated to JP,60-220147,A.

[0055]Have the structure of ingredient (a)-6 A-B-A, and The number average molecular weight 150000, molecular weight distribution 1.1, 18 % of the weight of the amounts of combined styrene, (a) 100% in 18 % of the weight of the total amounts of styrene by which the amount of styrene by which the content of the inner (A) block is contained in a block (A) 18% of the weight is contained in (a) (therefore) All the styrene polymerizes in a block (A), and a block (B) A polybutadiene block, The amount of 1,2-vinyl bonds of the polybutadiene part before hydrogenation compounded the hydrogenation block copolymer of the styrene / butadiene block copolymer which is 99% of a hydrogenation rate of a polybutadiene part 80% of the weight by the method indicated to JP,60-220147,A.

[0056]Adjustment of a solid catalyst; anhydrous  $\text{MgCl}_2$  and 49.5 g of dehydrated ethanol, 100 ml of vaseline oils, and 100 ml of silicone oils were stirred by nitrogen atmosphere-ization at 120 \*\* until  $\text{MgCl}_2$  dissolved thoroughly. Subsequently, this mixture was stirred for 3 minutes at 120 \*\* and 3000 rpm, after moving 150 ml of vaseline oils,

and 150 ml of silicone oils into 1500 ml of autoclave put in beforehand. It added in 1000 ml of n-heptane which had this mixture cooled, and under stirring, and the spherical solid of  $\text{MgCl}_2$  and 3EtOH was

deposited (mean particle diameter of 30-150 micrometers). It dried carrying out temperature up of the solid furthermore obtained to 100 °C from 50 °C under a nitrogen atmosphere, and adjusted to the EtOH/ $\text{MgCl}_2$  mole ratio 1.27. The obtained solid had porosity [ of 0.139cc/g ],

and surface area 9.1m<sup>2</sup>/g, and 0.564g/cc of bulk density.

[0057]25 g of this solid (carrier) was added under 0 °C and a nitrogen atmosphere in the autoclave with stirring into which  $\text{TiCl}_4$  625cc was put beforehand. Furthermore, temperature up of this autoclave was carried out to 100 °C over 1 hour. the time of temperature becoming 40 °C in a temperature-up course -- diisobutyl phthalate -- 1/8 time mole-ratio addition of magnesium -- it carried out. It settled after 2-hour stirring and at the temperature at 100 °C, and the solid was settled. The siphon attracted and removed supernatant liquid.  $\text{TiCl}_4$  550ml was newly added

and it settled after 1-hour stirring at 120 °C. The room temperature washed the solid which remained supernatant liquid after suction removal by the siphon 3 times 6 times at 60 °C using 200 ml of anhydrous hexane. It was used as a catalyst for a polymerization of an ingredient (b) after desiccation under vacuum.

[0058]Ingredient (b)-1 and ingredient (b)-2 were polymerized by the following method. The polymerization was continuously performed in a series of reactors provided with the device transported to the following reactor one by one from one reactor. In 22 l. of autoclave with stirring, liquid propylene at 20 °C 16 l., And the polymerization catalyst (aluminum/CMMS mole ratio 7.5) which consists of a mixture of about 0.15 g of the above-mentioned solid catalysts, and triethylaluminum 10% of hexane solutions [ 75 ml of ] and cyclohexyl methyldimethoxysilane (CMMS) was added, and it was made to polymerize for 24 minutes at 20 °C. Subsequently, this prepolymer was sent to the first reactor in the gaseous phase, and homopolymerization of propylene was performed there. Furthermore, this polymer was moved to the second reactor, and copolymerization of ethylene and propylene was performed there. The polymerization conditions of the first and the second reactor and the acquired description of the final product were shown in Table 1.

[0059]

[Table 1]

表 1

		成分 (b) - 1	成分 (b) - 2
第一 反 応 器	温度 (℃)	7 0	7 0
	圧力 (a t m)	3 0	3 0
	重合時間 (分)	3 0	3 0
	気相中の水素 (モル%)	6	2
	イソタクチック指数 (重量%)	9 5 . 5	9 5 . 4
第二 反 応 器	温度 (℃)	5 0	5 0
	圧力 (a t m)	1 4	1 4
	時間 (分)	2 5 0	2 5 0
	気相中の水素 (モル%)	7	4
	気相中のエチレン (モル%)	1 9 . 5	2 3 . 5
最 終 生 成 物	収量 (重合体K g / 触媒g)	7 . 5	8 . 3
	エチレン含量 (w t %)	2 2 . 5	3 0 . 1
	ホモポリプロピレン量 (w t %)	4 3 . 0	2 8 . 5
	融点 (℃)	1 6 4	1 6 3
	曲げ弾性率 (M P a)	1 0 3	8 3
	ショアD硬さ	4 3	4 0
	MFR (g / 1 0 分)	2 8	1 2
ゴムの平均分散粒径 (μ m)		0 . 4	0 . 5

[0060]Made in ingredient (b)-3 Montel, KYATAROI Adflex KS-084P, MFR30g/10 minutes. Flexural-modulus 108MPa, the Shore D hardness 44, mean-dispersion particle diameter of 0.4 micrometer of rubber.

[0061]Made in ingredient (b)-4 Montel, KYATAROI Adflex KS-359P, MFR12g/10 minutes. Flexural-modulus 83MPa, the Shore D hardness 41, mean-dispersion particle diameter of 0.6 micrometer of rubber.

[0062]Made in ingredient (b)-5 Montel, KYATAROI Adflex KS-221P, MFR2.5g/10 minutes. Flexural-modulus 350MPa, the Shore D hardness 53, mean-dispersion particle diameter of 0.5 micrometer of rubber.

[0063] Ingredient (c)

The Idemitsu Kosan make, paraffin series oil. Diana process oil PW-380 (kinetic viscosity; 380cSt).

[0064] Ingredient (d)

The product made from JPO, show AROMAMK511 (block type polypropylene), MFR15g/10 minutes. After blending with a Henschel mixer at each rate shown in Table 1 as the flexural-modulus 1400MPa example 1 - a 4 hydrogenation block copolymer using (b)-1 as (a)-2 and a polypropylene mixture, Melt kneading was carried out on 220 \*\* conditions with the direction twin screw extruder of the diameter of 45 mm, and the pellet of the elastomer composition was obtained. The result of physical properties and shaping molding workability was shown in Table 2.

[0065](a)-2, (a)-6, and (a)-7 are used as the comparative example 1 - a 5 hydrogenation block copolymer, Santoprene 203-40 (the rate of bending flexibility -- 80 MPa) which it extrudes as (b)-1 and comparison as a polypropylene mixture, and is blend type TPO (PP/EPDM blend) Using the distributed particle diameter of 9 micrometers of rubber, it kneaded like the method of Examples 1-4, and evaluated for the Shore D hardness 40 and MFR8g/10 minutes. The result was shown in Table 2. It is clear from this result that the constituent's besides the range of this invention

one of physical properties is bad.

[0066]

[Table 2]

表 2

		実施例 1	実施例 2	実施例 3	実施例 4
組成	(a) 成分	(a)-2	(a)-2	(a)-2	(a)-2
	水添ブロック共重合体	1 0 0	1 0 0	1 0 0	1 0 0
重量部	(b) 成分	(b)-1	(b)-1	(b)-1	(b)-1
	プロピレン混合物	2 0	5 0	1 0 0	2 0 0
物性	MFR (g/10分)	7	8	9	1 4
	硬さ (JIS A)	6 5	7 1	7 4	9 0
	引張強さ (MPa)	9 . 4	1 0 . 0	1 0 . 5	1 1 . 3
	伸び (%)	9 8 0	8 6 0	8 0 0	7 5 0
	反撥弾性 (%)	5 5	5 0	4 5	4 0
シボ落ち試験		○	○	○	○
耐傷付き性 光沢保持率 (%)		9 7	9 6	9 6	9 0
成形加工性		○	○	○	○

[0067]

[Table 3]

表 3

		比較例 1	比較例 2	比較例 3	比較例 4
組成	(a) 成分	(a)-2	(a)-2	(a)-2	(a)-6
	水添ブロック共重合体	1 0 0	1 0 0	1 0 0	1 0 0
重量部	(b) 成分	(b)-1	(b)-1	Santoprene203-40	(b)-1
	プロピレン混合物	—	9 5 0	1 0 0	1 0 0
物性	MFR (g/10分)	2	2 5	2	6
	硬さ (JIS A)	4 6	9 6	7 5	8 3
	引張強さ (kgf/cm <sup>2</sup> )	9 . 4	1 1 . 6	5 . 8	1 4 . 0
	伸び (%)	9 8 0	8 0 0	6 0 0	8 5 0
	反撥弾性 (%)	5 8	3 2	3 8	5 8
シボ落ち試験		×	○	○	○
耐傷付き性 光沢保持率 (%)		9 9	6 2	2 5	6 5
成形加工性		×	○	×	△

[0068](a)-1, (a)-2, (a)-3, (a)-4, (a)-5, and (a)-6 are used as Example 5 - an 11 hydrogenation block copolymer, After blending with a Henschel mixer at each rate shown in Table 4, using (b)-1, (b)-2, (b)-3, and (b)-4 as a polypropylene mixture, melt kneading was carried out on 220 \*\* conditions with the direction twin screw extruder of the diameter of 45 mm, and the pellet of the elastomer composition was obtained. Next, the pellet of this elastomer composition was fabricated and the result was shown in Table 4 and Table 5. The elastomer of this invention is excellent in a sex with a crack-proof, intensity, and heat resistance, and

that of the melting characteristic is good, and its excelling in injection-molding nature is clearer than this result.

[0069]

[Table 4]

表 4

		実施例 5	実施例 6	実施例 7	実施例 8
組成	(a) 成分	(a)-1	(a)-3	(a)-4	(a)-5
	水添ブロック共重合体	1 0 0	1 0 0	1 0 0	1 0 0
重量部	(b) 成分	(b)-1	(b)-1	(b)-1	(b)-1
	ポリプロピレン混合物	1 0 0	1 0 0	1 0 0	1 0 0
物性	MFR (g/10分)	1 8	4. 2	1 2	1 3
	硬さ (J I S A)	8 0	7 3	7 8	7 2
	引張強さ (kgf/cm <sup>2</sup> )	5. 5	1 5. 2	1 2. 5	1 0. 3
	伸び (%)	6 5 0	9 8 0	7 5 0	1 0 4 0
	耐傷付き性	9 1	9 8	9 4	9 7
	光沢保持率 (%)				
シボ落ち試験		○	○	○	○
成形加工性		○	○	○	○

[0070]

[Table 5]

表 5

		実施例 9	実施例 10	実施例 11
組成	(a) 成分	(a)-2	(a)-2	(a)-2
	水添ブロック共重合体	1 0 0	1 0 0	1 0 0
重量部	(b) 成分	(b)-2	(b)-3	(b)-4
	ポリプロピレン混合物	1 0 0	1 0 0	1 0 0
物性	MFR (g/10分)	6	1 1	7
	硬さ (J I S A)	6 5	7 3	7 0
	引張強さ (kgf/cm <sup>2</sup> )	8. 2	1 0. 0	8. 5
	伸び (%)	9 5 0	9 7 0	9 6 0
	耐傷付き性	9 5	9 8	9 7
	光沢保持率 (%)			
シボ落ち試験		○	○	○
成形加工性		○	○	○

[0071](a)-2, (a)-4, and (a)-5 are used as Example 12 - an 18 hydrogenation block copolymer, Using (b)-3 and (b)-4 as a propylene mixture, using (c) as a hydrocarbon oil, it kneaded like the method of Examples 5-12, and each rate shown in Table 6 and Table 7 estimated, using (d) as polyolefin system resin. The result was shown in Table 6 and Table 7. The elastomer of this invention is excellent in a sex with a crack-proof, intensity, and heat resistance, and that of the melting characteristic is good, and its excelling in injection-molding nature is clearer than this result.

[0072]

[Table 6]

表 6

		実施例12	実施例13	実施例14	実施例15
組成重量部	(a) 成分	(a)-2	(a)-2	(a)-2	(a)-4
	水添ブロック共重合体	100	100	100	100
	(b) 成分	(b)-3	(b)-3	(b)-3	(b)-3
	ポリプロピレン混合物	100	100	100	100
重量部	(c) 成分	(c)	(c)	(c)	(c)
	炭化水素油	40	—	40	40
	(d) 成分	(d)-1	(d)-1	(d)-1	(d)-1
	ポリオレフィン系樹脂	—	70	70	70
物性	MFR (g/10分)	14	10	22	6
	硬さ (JIS A)	61	93	86	85
	引張強さ (kgf/cm <sup>2</sup> )	6.9	10.8	7.6	14.5
	伸び (%)	900	720	730	800
	耐傷付き性	93	92	95	92
	光沢保持率 (%)				
シボ落ち試験		○	○	○	○
成形加工性		○	○	○	○

[0073]

[Table 7]

表 7

		実施例16	実施例17	実施例18
組成重量部	(a) 成分	(a)-5	(a)-2	(a)-2
	水添ブロック共重合体	40	40	40
	(b) 成分	(b)-3	(b)-3	(b)-4
	ポリプロピレン混合物	60	60	60
重量部	(c) 成分	(c)	(c)	(c)
	炭化水素油	40	40	40
	(d) 成分	(d)-2	(d)-2	(d)-2
	ポリオレフィン系樹脂	85	70	70
物性	MFR (g/10分)	8.5	6.0	6.5
	硬さ (JIS A)	96	85	86
	引張強さ (kgf/cm <sup>2</sup> )	120	115	113
	伸び (%)	730	770	770
	耐傷付き性	89	79	78
	光沢保持率 (%)			
シボ落ち試験		○	○	○
成形加工性		○	○	○

[0074]

[Effect of the Invention] Since the elastomer composition obtained by this invention is excellent in a sex with a crack-proof, intensity, heat resistance, pliability, and molding workability, can use it suitably in the field of autoparts, household appliance parts, a toy, general merchandise, etc., but. Since it excels in a sex with a crack-proof especially, it can be used conveniently for automobile exterior parts, such as automobile interior parts which need product appearance, such as an instrument panel, an armrest, a handle, and a phon pad, a wind mall, a bumper. Since it excels in the sex with a crack-proof on the surface of mold goods, and molding workability and the painting process which was necessity conventionally can be abolished, a high throughput and low



cost are realized.

[Translation done.]